coefficients. A decrease of the ratio of the volumes of the gas compartment with respect to the liquid compartment would increase the suitability of the present cell for systems with very low gas solubilities, as in the present configuration the accuracy of the pressure transducer tends to become limiting in the case of low absolute pressure decreases. For systems with high gas solubilities in combination with high diffusivities, a thicker diaphragm offers the possibility to determine more exactly the initial conditions and therefore facilitates experimentation.

4. Conclusions

A modified diaphragm cell has been developed for the measurement of diffusion coefficients of gases in liquids. The diaphragm cell is operated batchwise with respect to both gas and liquid phases, and the absorption process is followed by means of the gas pressure decrease which is recorded by a pressure transducer.

The present diaphragm cell was shown to be very suitable for the determination of diffusion coefficients at higher temperatures.

The diffusion coefficients of CO_2 and propene in toluene have been measured at temperatures ranging from 298 to 328 K. The diffusivity for various other gas-liquid systems has been determined at 298 K.

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Glossary

A	diaphragm surface area
C	concentration
D	diffusion coefficient
f	proportionality factor (eq 6)
k	mass transfer coefficient
m	dimensionless solubility
t	time
T	temperature
V	volume

Greek Letters

δ	diaphragm thickness
ϵ	porosity
γ	porosity/tortuosity factor ($\gamma = \epsilon/\tau$)
τ	tortuosity

Subscripts / Superscripts

eff	effective
g	gas phase
L	liquid phase

Registry No. CO_2, 124-38-9; N_2O, 10024-97-2; N_2, 7727-37-9; propene, 115-07-1; toluene, 108-88-3; chlorobenzene, 108-90-7.

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Surface Tension Measurements of Glycerol with Organic Cosolvents

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Surface tension data of binary mixtures of glycerol with methanol, 1-propanol, acetic acid, propionic acid, dimethyl sulfoxide, and *N,N*-dimethylformamide have been measured with a Du Nöuy torsion balance by a ring-detachment method. The values of the excess surface tension for these mixtures were also calculated.

1. Introduction

The literature dealing with the surface tension of binary mixtures is extensive (*1-3*). Such systems involving alcohols are interesting because of their inherent nature of forming associations in the form of hydrogen bonds within themselves or with other components. This property is directly reflected in various physical parameters, such as densities (*4*), viscosities (*5*), and surface tensions (*6*).

The aim of this paper is to determine the surface tension values of binary mixtures of glycerol with organic cosolvents, e.g. methanol, 1-propanol, acetic acid, propionic acid, dimethyl sulfoxide, and *N,N*-dimethylformamide. The values of the excess surface tension for these binary mixtures have also been computed.

2. Experimental Section

The chemicals used in this work were methanol (99.8%), 1-propanol (99.5%), acetic acid (99.8%), *N,N*-dimethylformamide (99.5%), and dimethyl sulfoxide (99.5%), which were supplied by E. Merck, and propionic acid (99%) and glycerol (99.5%) were supplied by BDH. Methanol and 1-propanol were

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Table I. Surface Tension ($\sigma/(10^{-3}\ \mathrm{N\ m^{-1}})$) and the Excess Surface Tension ($\sigma^E/(10^{-3}\ \mathrm{N\ m^{-1}})$) of the Binary Mixtures of Glycerol with Organic Cosolvents (Mole Fraction, *X*) at 298.15 K

X	σ	σ^E	*X*	σ	σ^E
Methanol					
1.0000	22.0	0.0	0.6542	33.5	-2.5
0.9620	26.0	2.9	0.5525	36.0	-4.1
0.9197	27.0	1.8	0.4177	40.5	-5.1
0.8677	28.5	1.4	0.2429	44.0	-8.7
0.8123	30.0	0.4	0.0000	62.5	0.0
0.7418	32.0	-0.5			
1-Propanol					
1.0000	23.0	0.0	0.5078	29.0	-13.4
0.9321	24.0	-1.7	0.3957	30.5	-16.4
0.8595	25.5	-3.1	0.2771	32.0	-19.6
0.7806	26.5	-5.2	0.1495	41.5	-15.1
0.6969	27.5	-7.5	0.0000	62.5	00.0
0.6042	28.0	-10.6			
Acetic Acid					
1.0000	27.0	0.0	0.5060	39.5	-5.0
0.9316	29.0	-0.4	0.3962	43.5	-4.9
0.8586	31.0	-1.0	0.2766	47.5	-5.2
0.7808	33.0	-1.8	0.1654	52.0	-4.6
0.6971	35.5	-2.3	0.0000	62.5	0.0
0.6037	36.0	-5.1			
Propionic Acid					
1.0000	25.5	0.0	0.4399	36.5	-9.7
0.9318	27.5	-0.5	0.3358	38.5	-12.1
0.8230	30.0	-2.1	0.2434	40.5	-13.0
0.7328	32.0	-3.4	0.1159	47.0	-11.2
0.6385	33.0	-5.9	0.0000	62.5	0.0
0.5408	35.0	-7.5			
N,N-Dimethylformamide (DMF)					
1.0000	34.0	0.0	0.4639	46.5	-2.8
0.9184	36.0	-0.8	0.3544	49.0	-3.4
0.8346	39.0	+0.3	0.2423	51.5	-4.1
0.7474	41.0	-0.2	0.1493	53.5	-4.2
0.6568	43.5	-0.3	0.0000	62.5	0.0
0.5638	45.0	-1.4			
Dimethyl Sulfoxide (DMSO)					
1.0000	42.5	0.0	0.4413	52.5	-1.2
0.9083	43.5	-0.8	0.3357	54.5	-1.3
0.8246	44.5	-1.5	0.2276	58.0	-0.1
0.7329	46.0	-1.8	0.1159	60.0	-0.2
0.6374	48.0	-1.7	0.0000	62.5	0.0
0.5429	51.0	-0.6			

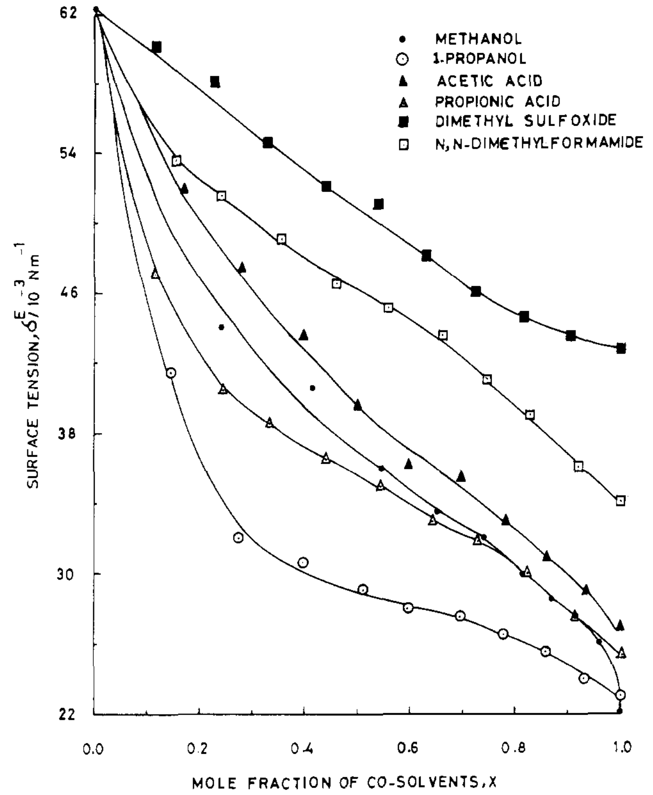

Figure 1. Plot of surface tension, σ, versus mole fraction of organic cosolvents, *X*.

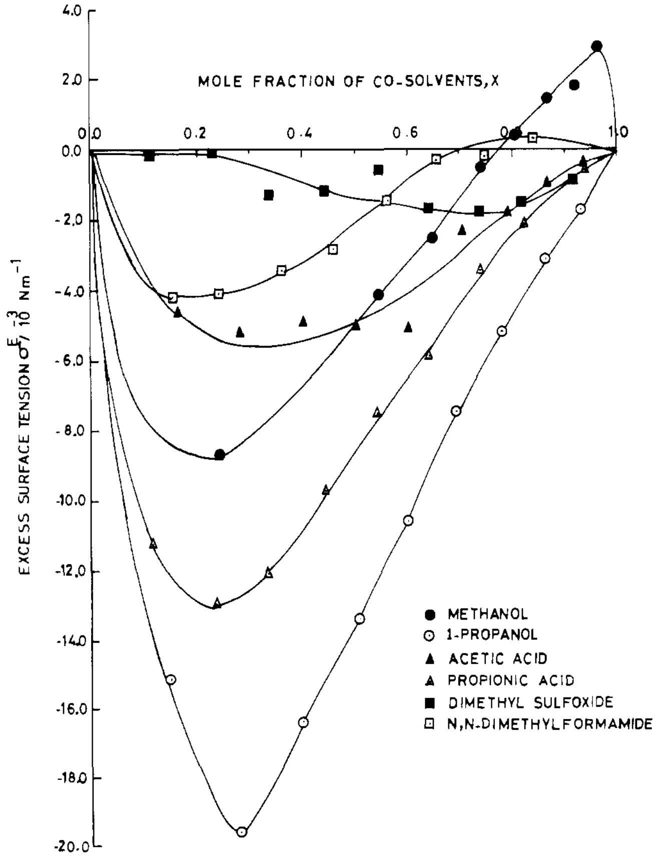

Figure 2. Plot of the excess surface tension, σ^E, versus mole fractions of organic cosolvents, *X*.

further dried overnight over anhydrous calcium chloride, refluxed for 8 h, and finally distilled with the middle fraction being collected. The distillates were stored in a dessicator containing anhydrous calcium chloride. However, acetic acid, propionic acid, dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF), and glycerol were used as received.

The refractive indexes and densities of the liquids were determined at 298.15 ± 1 K. Infrared spectra of the liquids showed that a negligible amount of moisture (<0.5%) may be present.

Mixtures of all component liquids with glycerol were prepared by weighing appropriate amounts of each solvent in glass stoppered flasks. The balance precision was $\pm 1 \times 10^{-4}$ g. The accuracy of the mole fractions was estimated to be within ±0.0004. The surface tension of the samples were measured by a ring-detachment method (*7*) using a Du Nöuy torsion balance. The platinum ring (4 cm in circumference) was thoroughly cleaned and flame-dried before each measurement. The torsion balance was calibrated with conductivity-grade water. The temperature was monitored by a Beckman thermometer, and all the measurements were performed at room temperature maintained at 298.15 ± 1 K and at atmospheric pressure. No attempt was made to monitor the relative humidity of the air to which the sample was exposed for a short period of time during measurements. However, any effect of humidity on the composition of mixtures was considered to be negligible. The reproducibility of replicate measurements on the same sample was within ±0.5%.

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3. Results and Discussion

The measured values of surface tension and the computed values of the excess surface tension for binary mixtures of glycerol and organic cosolvents are reported in Table I. Plots of the surface tension versus mole fraction of cosolvents, shown in Figure 1, indicate that the surface tension of all the binary mixtures investigated here decreases with an increase of the cosolvent mole fraction.

The excess surface tension, σ^E, may be defined as

$$\sigma^E = \sigma - (\sigma_1 X_1 + \sigma_2 X_2) \tag{1}$$

where σ is the surface tension of the mixture and σ_1 and σ_2 are surface tensions of the two components of mole fractions X_1 and X_2, respectively.

The values of σ^E for various mole fractions of cosolvents are shown in Table I and graphically shown in Figure 2. All these mixtures, except DMSO, show minima in σ^E values below a 0.3 mole fraction of the cosolvent. The minimum in the DMSO/glycerol mixture is observed at a 0.75 mole fraction of DMSO. Positive excess mixing is also observed in methanol and DMF mixtures near 0.9 mole fractions of the cosolvents.

Registry No. DMSO, 67-68-5; DMF, 68-12-2; glycerol, 56-81-5; methanol, 67-56-1; propanol, 71-23-8; acetic acid, 64-19-7; propionic acid, 79-09-4.

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Excess Volumes and Isentropic Compressibilities of Mixtures of *p*-Chlorotoluene + 2-Propanol, + 2-Methyl-1-propanol, and + 3-Methyl-1-butanol at 303.15 K

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Excess volumes and isentropic compressibilities of binary mixtures of *p*-chlorotoluene with 2-propanol, 2-methyl-1-propanol, and 3-methyl-1-butanol have been measured at 303.15 K. The excess volume exhibits inversion in sign in the three mixtures. The results have been compared with those of the three corresponding 1-alkanols. V^E is more positive for the 1-alkanols group. Deviation in isentropic compressibility, the difference between the value of the function for the real mixture and that for the ideal mixture, is negative over the whole range of composition in the three mixtures.

Introduction

We report measurements of excess volumes and isentropic compressibilities for three binary mixtures. The mixtures are *p*-chlorotoluene + 2-propanol, + 2-methyl-1-propanol, and + 3-methyl-1-butanol. The results have been compared with those reported in the literature (*1*) for mixtures of *p*-chlorotoluene with the corresponding 1-alkanols. The comparison was made to determine the effect of the change in environment of the OH function on the two properties.

Experimental Section

Excess volumes were measured directly using the dilatometer described by Rao and Naidu (*2*). The mixing cell contained two bulbs of different capacities which were connected through a U tube with mercury to separate the two components. One end of the bulb was fitted with a capillary (1-mm i.d.), and the other end of the second bulb was fitted with a ground-glass stopper. The excess volumes were accurate to ±0.003 $cm^3\ mol^{-1}$. Isentropic compressibilities were computed from measured sound speed data and densities calculated from the excess volumes.

Table I. Densities (ρ) of Pure Components at 303.15 K

	ρ/(g cm^{-3})		
component	lit. (*5*)	present study	accuracy
2-propanol	0.776 90	0.776 85	±0.000 05
2-methyl-1-propanol	0.794 37	0.794 34	±0.000 03
3-methyl-1-butanol	0.801 79	0.801 82	±0.000 03

The ultrasonic sound speed was measured with a single-crystal interferometer at 4 MHz, and the results were accurate to ±0.15%. All the measurements were made at constant temperature employing a thermostat that could be maintained to ±0.01 K.

Purification of Materials

All the materials were purified by the methods described by Riddick and Bunger (*3*) and Vogel (*4*). *p*-Chlorotoluene (E. Merck) was washed successively with 30 cm^3 of (10% by mass) sodium hydroxide solution and an equal amount of concentrated sulfuric acid and water. It is dried with anhydrous calcium chloride, decanted, and distilled. All alcohols were dried by refluxing with fused calcium oxide and finally distilled using a fractionating column.

The purity of the samples was checked by comparing the measured densities of the compounds with those reported in the literature (*5*, *6*). Densities were determined with a bicapillary type pycnometer, which offered an accuracy of 2 parts in 10^5. The measured densities and those reported in the literature (*5*) are given in Table I. The density for *p*-chlorotoluene was available at 298.15 K in the literature (*6*). The

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