their values for tracer diffusion coefficient at infinite dilution for pyridine (0.5×10^{-5} cm^2 s^{-1} at 13 °C and 0.875×10^{-5} cm^2 s^{-1} at 25 °C) and water (1.175×10^{-5} cm^2 s^{-1} at 13 °C and 1.58×10^{-5} cm^2 s^{-1} at 25 °C), respectively.

The concentration-dependent D_{12} calculated by using eq 4 and the activity data of Ewerth (*16*) are also shown in Figure 4 and seem to be in relatively good agreement with the experimental values.

Glossary

a_i	activity for component *i*
A_i	constants for eq 2
B_i	constants for eq 3
D_{12}	mutual diffusion coefficient, cm^2 s^{-1}
$D_{12}{}^0$	limiting diffusion coefficient for component 1 in component 2, cm^2 s^{-1}
$D_{21}{}^0$	limiting diffusion coefficient for component 2 in component 1, cm^2 s^{-1}
D_f	fundamental diffusion coefficient, cm^2 s^{-1}
f^{th}	thermodynamic factor
K	autocorrelation function
n^D	refractive index
s	exponent to thermodynamic factor
t_c	decay time
x_i	mole fraction of component *i*
$\sigma(n^D)$	standard deviation for refractive indices
$\sigma(D_{12})$	standard deviation for mutual diffusion coefficients, cm^2 s^{-1}

Registry No. CCl$_4$, 56-23-5; CS$_2$, 75-15-0; cyclohexane, 110-82-7; toluene, 108-88-3; pyridine, 110-86-1; water, 7732-18-5.

Literature Cited

(1) Gulari, E.; Brown, R. J.; Pings, C. J. *AIChE J.* **1973**, *19*, 1196.
(2) Czworniak, K. J.; Andersen, H. C.; Pecora, R. *Chem. Phys.* **1975**, *11*, 451.
(3) Krahn, W.; Schweiger, G.; Lucas, K. *J. Phys. Chem.* **1983**, *87*, 4515.
(4) Carman, P. C.; Stein, L. H. *Trans. Faraday Soc.* **1956**, *52*, 619.
(5) Rathbun, R. E.; Babb, A. L. *Ind. Eng. Chem. Process Des. Dev.* **1966**, *5*, 273.
(6) Vignes, A. *Ind. Eng. Chem. Fundam.* **1966**, *5*, 189.
(7) Gainer, J. L. *Ind. Eng. Chem. Fundam.* **1970**, *9*, 381.
(8) *Leffler*, J.; Cullinan, H. T. *Ind. Eng. Chem. Fundam.* **1970**, *9*, 84.
(9) Kosanovich, G. M.; Cullinan, H. T. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 41.
(10) Cussler, E. L. *AIChE J.* **1980**, *26*, 43.
(11) Hayduk, W.; Minhas, B. S. *Can. J. Chem. Eng.* **1982**, *60*, 295.
(12) Hlavaty, K. *Collect. Czech. Chem. Commun.* **1970**, *35*, 2878.
(13) *Bernatova*, S.; Boublik, T. *Collect. Czech. Chem. Commun.* **1977**, *42*, 2615.
(14) Schmidt, G. C. *Z. Phys. Chem.* **1926**, *121*, 221.
(15) *Brun*, B.; Salvinien, J. *J. Chim. Phys.* **1967**, *64*, 1319.
(16) Ewerth, M. *Bull. Soc. Chim. Belg.* **1936**, *45*, 493.

Received for review February 3, 1986. Revised June 24, 1986. Accepted August 7, 1986. This work was supported by the Arbeitsgemeinschaft industrieller Forschungsvereinigungen e. V. by a grant of the Bundesministerium für Wirtschaft, F.R.G., which is gratefully acknowledged.

Viscosities of Binary Liquid Mixtures

T. M. Aminabhavi,* L. S. Manjeshwar, and R. H. Balundgi

Department of Chemistry, Karnatak University, Dharwad 580 003, India

Measurements of viscosities for 21 binary mixtures at 25 °C are reported. The results are interpreted in terms of the nature of the interacting species in the mixture. Although viscosity data have been reported for a few systems in the literature, the 21 systems studied in this work were chosen because of the variety of interaction types.

Introduction

As part of a general research program (*1*, *2*) to accumulate experimental data on binary liquid mixtures, we now present viscosity data on 21 mixtures comprising of bromoform, carbon tetrachloride, dimethyl sulfoxide, cyclohexane, bromobenzene, dimethylformamide, methyl ethyl ketone, ethyl acetate, methanol, nitromethane, benzene, and *p*-xylene. Viscosities were measured over the entire composition scale at 25 °C, and the results are discussed in terms of the nature of interacting species in the mixture.

Experimental Section

The solvents used in this study were of reagent grade. All of the solvents were purified by fractionating through a 5-ft. column. Gas chromatography of these solvents did not detect any impurities except cyclohexane wherein the mole percent impurity varied between 0.04 and 0.06. The boiling points and viscosities of the samples finally selected for investigation (shown in Table I) agreed well with the corresponding values quoted in the literature. Particular care was taken in handling the hygroscopic liquids as the slightest traces of water were found to affect the data of pure solvents quite markedly.

Table I. Data for Pure Components at 25 °C

solvent	boiling point, °C found	lit.	ref	viscosity, kg/m·s found	lit.	ref
benzene	80.00	80.10	(*4*)	0.0601	0.0599	(*4*)
carbon tetrachloride	76.2	76.75	(*4*)	0.0892	0.0902	(*4*)
cyclohexane	80.10	80.74	(*4*)	0.0883	0.0886	(*4*)
bromoform	149.00	149.5	(*7*)	0.1873	0.1890	(*7*)
methyl ethyl ketone	79.00	79.6	(*7*)	0.0475	0.0480	(*5*)
dimethyl sulfoxide	190.00	189.85	(*7*)	0.2024	0.2021	(*6*)
ethyl acetate	77.10	77.26	(*5*)	0.0439	0.0424	(*8*)
methanol	64.20	65.15	(*7*)	0.0590	0.0547	(*7*)
nitromethane	100.2	100.8	(*7*)	0.0627	0.0620	(*7*)
dimethylformamide	152.80	153.00	(*7*)	0.0805	0.0800	(*9*)
bromobenzene	155.90	156.05	(*5*)	0.1081	0.1040	(*9*)
p-xylene	137.50	138.00	(*9*)	0.0615	0.0600	(*9*)

Solvent mixtures were prepared for several compositions. Mixtures were made by weighing an appropriate volume of each solvent. To minimize the preferential evaporation of one of the solvents in the mixture we used special airtight bottles. When once these mixtures were prepared, all the measurements were done on the same day. However, keeping the mixtures overnight and remeasuring them on the following day indicated an error of 0.5–1.5% in viscosity.

The viscosities were measured at 25 °C with an Ostwald viscometer by comparing the flow times of pure liquid or the

0021-9568/87/1732-0050$01.50/0

Table II. Viscosity (η) Data for Binary Solvent Mixtures at 25 °C

x_1	η, kg/m·s	x_i	η, kg/m·s	x_1	η, kg/m·s
(I) Bromoform (1)–Carbon Tetrachloride (2)					
0.0	0.0892	0.4431	0.1231	0.8068	0.1609
0.1194	0.0965	0.5248	0.1308	0.8986	0.1753
0.2186	0.1307	0.6217	0.1397	1.0	0.1873
0.3128	0.1115	0.7153	0.1477		
(II) Bromoform (1)–Dimethyl Sulfoxide (2)					
0.0	0.2024	0.4446	0.2945	0.7553	0.2544
0.0899	0.2155	0.5453	0.2944	0.8619	0.2192
0.1708	0.2427	0.6466	0.2762	1.0	0.1873
0.3448	0.2816				
(III) Bromoform (1)–Cyclohexane (2)					
0.0	0.0883	0.5486	0.1258	0.8718	0.1670
0.1851	0.0959	0.6899	0.1409	1.0	0.1873
0.3428	0.1071				
(IV) Bromoform (1)–Bromobenzene (2)					
0.0	0.1081	0.5417	0.1510	0.8606	0.1769
0.1837	0.1207	0.6869	0.1627	1.0	0.1873
0.3369	0.1333				
(V) Bromoform (1)–Dimethylformamide (2)					
0.0	0.0805	0.4630	0.1794	0.8180	0.2016
0.1418	0.1075	0.6145	0.2007	1.0	0.1873
0.2704	0.1355	0.7144	0.2037		
(VI) Bromoform (1)–Methyl Ethyl Ketone (2)					
0.0	0.0475	0.5009	0.1072	0.8432	0.1626
0.1586	0.0583	0.6501	0.1318	1.0	0.1873
0.3052	0.0768				
(VII) Bromoform (1)–Ethyl Acetate (2)					
0.0	0.0439	0.5290	0.1141	1.0	0.1873
0.2713	0.0754	0.7683	0.1565		
(VIII) Carbon Tetrachloride (1)–Methanol (2)					
0.0	0.0590	0.4346	0.0844	0.7610	0.0858
0.1518	0.0719	0.5445	0.0874	0.8784	0.0867
0.2927	0.0809	0.6871	0.0875	1.0	0.0892
(IX) Carbon Tetrachloride (1)–Benzene (2)					
0.0	0.0601	0.4778	0.0744	0.8302	0.0842
0.1472	0.0655	0.6302	0.0790	1.0	0.0892
0.2844	0.0690				
(X) Carbon Tetrachloride (1)–Ethyl Acetate (2)					
0.0	0.0439	0.5010	0.0644	0.8438	0.0808
0.1581	0.0517	0.6498	0.0713	1.0	0.0892
0.3048	0.0570				
(XI) Carbon Tetrachloride (1)–Dimethylformamide (2)					
0.0	0.0805	0.4437	0.0958	0.8073	0.0949
0.1290	0.0879	0.5950	0.0966	1.0	0.0892
0.2556	0.0918				
(XII) Carbon Tetrachloride (1)–Cyclohexane (2)					
0.0	0.0883	0.5278	0.0836	0.8521	0.0860
0.1774	0.0847	0.6746	0.0844	1.0	0.0892
0.3265	0.0831				
(XIII) Carbon Tetrachloride (1)–Bromobenzene (2)					
0.0	0.1081	0.5187	0.0971	0.8522	0.0915
0.1709	0.1035	0.6674	0.0942	1.0	0.0892
0.3202	0.1011				
(XIV) Carbon Tetrachloride (1)–Methyl Ethyl Ketone (2)					
0.0	0.0475	0.4787	0.0648	0.8296	0.0792
0.1477	0.0485	0.6290	0.0697	1.0	0.0892
0.2858	0.0543				
(XV) Carbon Tetrachloride (1)–Dimethyl Sulfoxide (2)					
0.0	0.2024	0.4246	0.1654	0.8661	0.1067
0.1093	0.2001	0.5746	0.1500	1.0	0.0892
0.2260	0.1852	0.6402	0.1399		
(XVI) Carbon Tetrachloride (1)–Nitromethane (2)					
0.0	0.0627	0.3609	0.0702	0.7487	0.0805
0.0959	0.0636	0.5088	0.0751	1.0	0.0892
0.1961	0.0655				
(XVII) Dimethyl Sulfoxide (1)–Dimethylformamide (2)					
0.0	0.0805	0.5201	0.1242	0.8514	0.1785
0.1668	0.0924	0.6689	0.1474	1.0	0.2024
0.3195	0.1036				
(XVIII) Dimethyl Sulfoxide (1)–Nitromethane (2)					
0.0	0.0627	0.4320	0.1014	0.8120	0.1613
0.1135	0.0726	0.5943	0.1229	1.0	0.2024
0.2337	0.0823				
(XIX) Benzene (1)–Ethyl Acetate (2)					
0.0	0.0439	0.5324	0.0507	0.8535	0.0570
0.1715	0.0478	0.6702	0.0534	1.0	0.0601
0.3251	0.0489				
(XX) Benzene (1)–*p*–Xylene (2)					
0.0	0.0615	0.5839	0.0596	0.8802	0.0599
0.2099	0.0603	0.7205	0.0596	1.0	0.0601
0.3766	0.0596				
(XXI) Cyclohexane (1)–Methyl Ethyl Ketone (2)					
0.0	0.0475	0.4524	0.0501	0.8267	0.0685
0.1260	0.0426	0.6037	0.0554	1.0	0.0883
0.2633	0.0448				

mixture with that of double-distilled water. A Toshniwal constant temperature bath with a precision of ±0.01 °C was used. Triplicate measurements of each composition of the mixture showed reproducibility to within ±0.0005 kg/m/s for the viscosity measurements.

Viscosities were calculated from flow times which were measured in seconds for all the mixtures. Flow times for water as well as for pure solvents were quite consistent during the entire period of measurement. Only the average values of the viscosities from three independent measurements are presented in Table II. The mole fractions (x_i) of the liquids in the mixtures were calculated from the measured volumes and densities (*3*) of individual components.

Results and Discussion

Experimental viscosities are presented in Table II. The dependence of mixture viscosity on its composition is shown in Figure 1 for only a few representative mixtures. System II, bromoform–dimethyl sulfoxide, is particularly interesting in that it displays large positive deviations over the entire composition scale; the critical composition at which maximum occurs is around $x_1 \sim 0.5$. However, this trend was not seen with the bromoform–dimethylformamide mixture; the viscosity curve steadily increased all the way up to $x_1 \sim 0.6$ reaching maximum at around $x_1 \sim 0.71$ beyond which it further decreased slightly. Similarly, small positive deviations were seen for mixtures of carbon tetrachloride with either dimethylformamide or methanol. Small negative deviations were exhibited by mixtures of bromoform with carbon tetrachloride, cyclohexane, methyl ethyl ketone, or ethyl acetate. Even the mixtures of dimethyl sulfoxide with either nitromethane or dimethylformamide and mixtures of carbon tetrachloride with either nitromethane or ethyl acetate exhibited the same behavior. Two other mixtures which showed small negative deviations from straight-line behavior are benzene (1)–ethyl acetate (2) and cyclohexane (1)–methyl ethyl ketone (2). A linear dependence was prevalent for mixtures of benzene with either carbon tetrachloride or xylene and bromoform (1)–bromobenzene (2).

Grunberg (*4*) measured (at 25 °C) the viscosities of two mixtures, namely, carbon tetrachloride (1)–cyclohexane (2) and carbon tetrachloride (1)–benzene (2). Comparison of the present results with those of Grunberg shows a good agree-

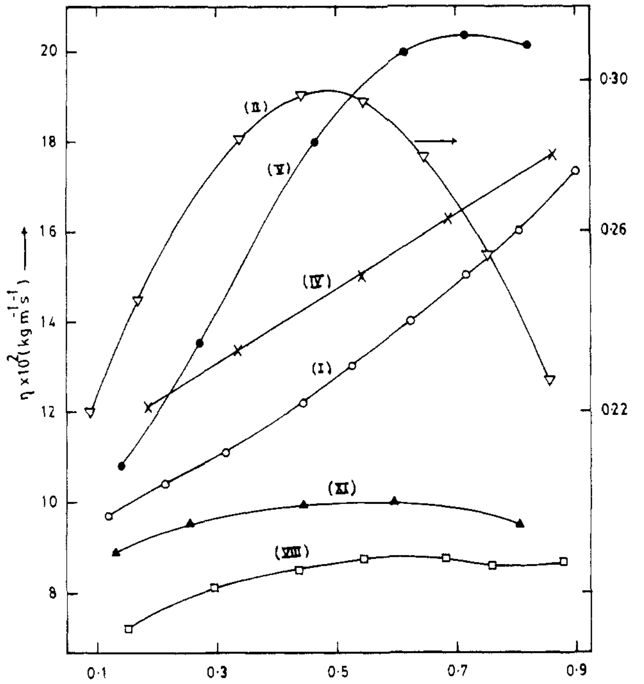

Figure 1. Viscosity vs. composition of the mixture. The numbers for the curves refer to systems mentioned in Table II.

ment. However, to our knowledge, no literature data on viscosities of binary mixtures containing bromoform were available and thus we could not compare the data with the literature findings.

Acknowledgment

T.M.A. thanks Professor P. E. Cassidy of Southwest Texas State University for the facilities provided during the preparation of this manuscript.

Registry No. Benzene, 71-43-2; carbon tetrachloride, 56-23-5; cyclohexane, 110-82-7; bromoform, 75-25-2; methyl ethyl ketone, 78-93-3; dimethyl sulfoxide, 67-68-5; ethyl acetate, 141-78-6; methanol, 67-56-1; nitromethane, 75-52-5; dimethylformamide, 68-12-2; bromobenzene, 108-86-1; *p*-xylene, 106-42-3.

Literature Cited

(1) Aminabhavi, T. M.; Patel, R. C.; Bridger, K.; Jayadevappa, E. S.; Prasad, B. R. *J. Chem. Eng. Data* **1982**, *27*, 125.
(2) Gokavi, G. S.; Raju, J. R.; Aminabhavi, T. M.; Balundgi, R. H.; Muddapur, M. V. *J. Chem. Eng. Data* **1986**, *31*, 15.
(3) Aminabhavi, T. M.; Manjeshwar, L. S.; Balundgi, R. H.; *Indian J. Chem.* **1986**, *25A*, 465.
(4) Grunberg, L. *Trans. Faraday Soc.* **1954**, *50*, 1293.
(5) Riddick, A. J.; Bunger, B. W. *Techniques of Chemistry*, 23rd ed.; Wiley-Interscience: New York, 1970; Vol. II.
(6) Fort, R. J.; Moore, W. R. *Trans. Faraday Soc.* **1966**, *62*, 1112.
(7) *CRC Handbook of Chemistry and Physics*, 64th ed.; Weast, R. C., Ed.; CRC: Boca Raton, FL, 1983-84.
(8) Timmermans, J. *Physico-Chemical Constants of Pure Organic Compounds*; Interscience: New York, 1950.
(9) Snyder, L. R.; Kirkland, J. J. *Introduction to Modern Liquid Chromatography*; Wiley: New York, 1976; Chapter 6.

Received for review January 16, 1986. Revised July 9, 1986. Accepted August 7, 1986.

Solubility Curves of Some Electrolytes (CF_3COONa, $NaClO_4$, $KClO_4$) in Molten 1,3-Dioxolan-2-one

Giancarlo Gioia Lobbia* and Gianfrancesco Berchiesi

Dipartimento Scienze Chimiche, Università di Camerino, 62032 Camerino, Italy

With the aim of investigating the interactions between an electrolyte and a nonaqueous solvent we present in this note the liquid–solid equilibria in the binary mixtures of 1,3-dioxolan-2-one (ethylene carbonate) and electrolytes.

Introduction

In previous papers (*1*–*8*) we showed that some amide solvents in mixtures with particular electrolytes (*3*) exhibit, with regard to crystallization, a peculiar behavior. The most probable explanation is the following: the presence of solutes stabilizes an open dimeric structure of the amide (*9*, *10*), which at low temperature (around the eutectic point) may polymerize giving these liquids a viscoelastic behavior in the ultrasonic frequency region (*11*–*13*).

Other liquids have been tested such as succinimide (*4*), but the crystallization behavior is not so anomalous as with low molecular weight amides. The behavior observed and the formation of polymeric structures are related (a) to the presence of cations (alkali or alkali earth) and anions derived from strong acids (*3*) and (b) probably to the possibility of hydrogen-bond formation (*4*). In order to check the latter point we investigated electrolyte solution behavior in $C_2H_4CO_3$, owing to the fact that this solvent cannot form hydrogen bonds.

Experimental Section

The experimental cryoscopic technique is reported in a previous paper (*14*). The 1,3-dioxolan-2-one (ethylene carbonate) (Fluka) is employed without further purification and dried under dynamic vacuum at room temperature. The following chemicals were used: $NaClO_4$ and $KClO_4$ (Erba), KCNS (Merck), NaCNS, HCOONa, and $NaNO_3$ (Fluka), CF_3COONa (Ega-Chemie). The purity of all the compounds employed was not less than 98%. These compounds were stored in a desiccator under dynamic vacuum.

Results and Discussion

The following electrolytes were employed as solutes: $NaNO_3$, HCOONa, NaCNS, KCNS, CF_3COONa, $KClO_4$, $NaClO_4$. Sodium nitrate, sodium formate, sodium thiocyanate, and potassium thiocyanate practically do not dissolve in ethylene carbonate. The others are soluble, and it was possible to measure liquid–