

Densities, Viscosities, and Refractive Indices of Bis(2-methoxyethyl) Ether + Cyclohexane or + 1,2,3,4-Tetrahydronaphthalene and of 2-Ethoxyethanol + Propan-1-ol, + Propan-2-ol, or + Butan-1-ol

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Densities, viscosities, and refractive indices for binary mixtures of bis(2-methoxyethyl) ether + cyclohexane at 298.15, 303.15, and 308.15 K and for those of bis(2-methoxyethyl) ether + 1,2,3,4-tetrahydronaphthalene and 2-ethoxyethanol + propan-1-ol, + propan-2-ol, or + butan-1-ol at 298.15, 303.15, 308.15, and 313.15 K are measured at 1 atm pressure as a function of mole fraction. The experimental results are used to calculate excess molar volume V^E , deviations in refractivity ΔR , based on the Lorentz-Lorenz relation, and deviations in viscosity $\Delta\eta$, of the mixtures. These results are fitted to a Redlich-Kister polynomial to estimate the binary interaction coefficients. The standard errors are calculated between the predicted and the experimental quantities.

Introduction

In previous papers from this laboratory, excess properties of mixtures of bis(2-methoxyethyl) ether, also known as diglyme, with esters (1-3), alkanes (4, 5), and alkanols (6) and those of 2-ethoxyethanol with *n*-alkanes (7) have been studied. In view of the importance of diglyme as a sonar transducer fill fluid in underwater navy research (8) and of 2-ethoxyethanol as a useful solvent in analytical research (9), more experimental data on the binary mixtures of these liquids are in order.

As a continuation of our general program of research concerning the physicochemical properties of binary organic liquid mixtures, we present here experimental results of density ρ , viscosity η , and refractive index n_D , for sodium D line for diglyme + cyclohexane, at 298.15, 303.15, and 308.15 K, and for diglyme + 1,2,3,4-tetrahydronaphthalene and mixtures of 2-ethoxyethanol with propan-1-ol, propan-2-ol, or butan-1-ol at 298.15, 303.15, 308.15, and 313.15 K, over the whole range of mixture composition at 1 atm pressure. The values of ρ , η , and n_D are used to calculate, respectively, the excess molar volume V^E and the deviations in viscosity $\Delta\eta$ and refractivity ΔR , the latter based on Lorentz-Lorenz relation (10, 11). These quantities are displayed graphically, and the results are fitted to a Redlich-Kister polynomial relation (12) using the Marquardt algorithm (13). The values of the estimated coefficients are tabulated along with the standard deviations between the experimentally calculated and the fitted quantities.

Experimental Section

Materials. The reagent grade bis(2-methoxyethyl) ether (B.D.H., Poole, England), cyclohexane (B.D.H. Laboratory, a division of Glaxo Laboratories Ltd., Bombay), 2-ethoxyethanol (E. Merck, Pvt. Ltd., Bombay), 1,2,3,4-tetrahydronaphthalene (Riedel, Germany), propan-1-ol, propan-2-ol, and butan-1-ol (all from S. D. Fine Chem. Pvt. Ltd., Bombay) were double-distilled before use. Their purities were checked by the constancy of their boiling temperatures during final distillations and also from a comparison of ρ , η , and n_D values with the literature findings (14-22) as given in Table 1. The GLC purity analyses using a

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Table 1. Comparison of Experimental Densities (ρ), Viscosities (η), and Refractive Indices (n_D) of Pure Liquids with the Literature Values at 298.15 K

| liquid (mol % purity) | $\rho/(\text{g}\cdot\text{cm}^{-3})$ | | $\eta/(\text{mPa}\cdot\text{s})$ | | n_D | |
|---------------------------------------|--------------------------------------|----------------|----------------------------------|---------------|--------|----------------|
| | exptl | lit. (ref) | exptl | lit. (ref) | exptl | lit. (ref) |
| diglyme (>99.4) | 0.9399 | 0.9397 (14) | 0.991 | 0.990 (15) | 1.4058 | 1.4060 (14) |
| cyclohexane (>99.6) | 0.7738 | 0.7739 (16) | 0.876 | 0.888 (17) | 1.4240 | 1.4235 (16) |
| 1,2,3,4-tetrahydronaphthalene (>99.6) | 0.9651 | 0.9662 (16) | 1.968 | 2.003 (18) | 1.5397 | 1.5392 (16) |
| 2-ethoxyethanol (>99.2) | 0.9259 | 0.9252 (18) | 1.838 | 1.850 (18) | 1.4054 | 1.4057 (18) |
| propan-1-ol (>99.6) | 0.7996 | 0.7996 (19) | 1.898 | 1.943 (18) | 1.3843 | 1.3843 (19) |
| propan-2-ol (>99.4) | 0.7809 | 0.7812 (19) | 1.936 | 2.052 (20) | 1.3747 | 1.3746 (19) |
| butan-1-ol (>99.6) | 0.8057 | 0.8058 (18) | 2.509 | 2.578 (21) | 1.3978 | 1.3973 (22) |

flame ionization detector (Nucon Series, Model 5700/5765, with fused silica columns) having a sensitivity better than 10^{-8} g of fatty acid/ μL of the solvent are also included in Table 1.

Binary mixtures were prepared by mixing appropriate volumes of liquids in specially designed ground glass airtight bottles and weighed in a single-pan Mettler balance (Switzerland, Model AE-240) to an accuracy of ± 0.01 mg. The possible errors in mole fractions are within ± 0.0001 .

Measurements. Densities of pure liquids and their binary mixtures were measured using a pycnometer (Lurex, NJ) having a bulb volume of 10 cm^3 and a capillary with an internal diameter of 1 mm. An average of triplicate measurements was considered, and these are accurate to $\pm 0.0002\text{ g}\cdot\text{cm}^{-3}$.

Viscosities were measured with a Cannon Fenske viscometer (size 100) supplied by Industrial Research Glassware, Ltd., NJ. An electronic stopwatch with a precision of ± 0.01 s was used to measure the liquid flow times. Triplicate measurements of flow times were reproducible within ± 0.01 s, and viscosities are accurate to $\pm 0.001\text{ mPa}\cdot\text{s}$.

Refractive indices for the sodium D line were measured with a thermostated Abbe refractometer (Bellingham and

Table 2. Experimental Densities (ρ), Viscosities (η), and Refractive Indices (n_D) of Binary Mixtures at Different Temperatures

| Diglyme (1) + Cyclohexane (2) | | Diglyme (1) + 1,2,3,4-Tetrahydronaphthalene (2) | | 2-Ethoxyethanol (1) + Propan-1-ol (2) | | 2-Ethoxyethanol (1) + Propan-2-ol (2) | | 2-Ethoxyethanol (1) + Butan-1-ol (2) | | | | | | | |
|-------------------------------|--------------------------|---|----------------------|---------------------------------------|--------------------------|---------------------------------------|----------------------|--------------------------------------|--------------------------|--------|----------------------|--------|--------------------------|--------|----------------------|
| x_1 | $\rho/(\text{gcm}^{-3})$ | n_D | $\eta/(\text{mPas})$ | x_1 | $\rho/(\text{gcm}^{-3})$ | n_D | $\eta/(\text{mPas})$ | x_1 | $\rho/(\text{gcm}^{-3})$ | n_D | $\eta/(\text{mPas})$ | x_1 | $\rho/(\text{gcm}^{-3})$ | n_D | $\eta/(\text{mPas})$ |
| 298.15 K | | | | | | | | | | | | | | | |
| 0.000 | 0.7737 | 1.4240 | 0.0000 | 0.9651 | 1.968 | 1.5397 | 0.0000 | 0.7996 | 1.898 | 1.3843 | 0.0000 | 0.7809 | 1.936 | 1.3747 | 0.0000 |
| 0.0981 | 0.7901 | 1.4205 | 0.1028 | 0.9623 | 1.786 | 1.5249 | 0.0969 | 0.8151 | 1.815 | 1.3868 | 0.1024 | 0.7991 | 1.858 | 1.3798 | 0.1017 |
| 0.1885 | 0.8058 | 1.4170 | 0.1977 | 0.9595 | 1.637 | 1.5115 | 0.1990 | 0.8307 | 1.761 | 1.3881 | 0.2002 | 0.8155 | 1.764 | 1.3822 | 0.2007 |
| 0.2854 | 0.8224 | 1.4146 | 0.3019 | 0.9565 | 1.500 | 1.4978 | 0.2917 | 0.8438 | 1.730 | 1.3924 | 0.3010 | 0.8319 | 1.703 | 1.3866 | 0.2996 |
| 0.3996 | 0.8421 | 1.4121 | 0.3993 | 0.9542 | 1.396 | 1.4841 | 0.3971 | 0.8583 | 1.659 | 1.3935 | 0.4035 | 0.8477 | 1.692 | 1.3887 | 0.4028 |
| 0.5024 | 0.8598 | 1.4107 | 0.5009 | 0.9516 | 1.294 | 1.4708 | 0.4928 | 0.8705 | 1.711 | 1.3959 | 0.5037 | 0.8623 | 1.682 | 1.3930 | 0.5032 |
| 0.6005 | 0.8761 | 1.4094 | 0.6660 | 0.9477 | 1.197 | 1.4496 | 0.5933 | 0.8827 | 1.721 | 1.3980 | 0.6022 | 0.8761 | 1.693 | 1.3950 | 0.6036 |
| 0.7027 | 0.8930 | 1.4090 | 0.7016 | 0.9468 | 1.144 | 1.4449 | 0.6923 | 0.8939 | 1.732 | 1.4004 | 0.6984 | 0.8889 | 1.711 | 1.3975 | 0.6986 |
| 0.8014 | 0.9087 | 1.4081 | 0.7949 | 0.9450 | 1.087 | 1.4334 | 0.7987 | 0.9055 | 1.754 | 1.4025 | 0.8009 | 0.9022 | 1.756 | 1.4028 | 0.8029 |
| 0.8980 | 0.9238 | 1.4073 | 0.8987 | 0.9422 | 1.032 | 1.4202 | 0.8853 | 0.9145 | 1.774 | 1.4032 | 0.9017 | 0.9143 | 1.773 | 1.4006 | 0.9000 |
| 1.0000 | 0.9399 | 1.4058 | 1.0000 | 0.9399 | 0.991 | 1.4058 | 1.0000 | 0.9259 | 1.838 | 1.4054 | 1.0000 | 0.9259 | 1.838 | 1.4054 | 1.0000 |
| 303.15 K | | | | | | | | | | | | | | | |
| 0.0000 | 0.7692 | 1.4186 | 0.0000 | 0.9611 | 1.778 | 1.5374 | 0.0000 | 0.7955 | 1.676 | 1.3816 | 0.0000 | 0.7765 | 1.731 | 1.3725 | 0.0000 |
| 0.0981 | 0.7854 | 1.4179 | 0.1028 | 0.9583 | 1.619 | 1.5226 | 0.0969 | 0.8111 | 1.607 | 1.3837 | 0.1024 | 0.7948 | 1.614 | 1.3766 | 0.1017 |
| 0.1885 | 0.8010 | 1.4144 | 0.1977 | 0.9553 | 1.487 | 1.5093 | 0.1990 | 0.8265 | 1.560 | 1.3860 | 0.2002 | 0.8110 | 1.540 | 1.3804 | 0.2007 |
| 0.2854 | 0.8176 | 1.4119 | 0.3019 | 0.9522 | 1.367 | 1.4957 | 0.2917 | 0.8396 | 1.542 | 1.3888 | 0.3010 | 0.8274 | 1.495 | 1.3831 | 0.2996 |
| 0.3996 | 0.8354 | 1.4096 | 0.3993 | 0.9498 | 1.275 | 1.4818 | 0.3971 | 0.8539 | 1.482 | 1.3919 | 0.4035 | 0.8432 | 1.490 | 1.3869 | 0.4028 |
| 0.5024 | 0.8549 | 1.4082 | 0.5009 | 0.9471 | 1.185 | 1.4683 | 0.4928 | 0.8660 | 1.521 | 1.3941 | 0.5037 | 0.8577 | 1.491 | 1.3900 | 0.5032 |
| 0.6005 | 0.8712 | 1.4071 | 0.6660 | 0.9430 | 1.071 | 1.4473 | 0.5933 | 0.8782 | 1.531 | 1.3968 | 0.6022 | 0.8716 | 1.504 | 1.3928 | 0.6036 |
| 0.7027 | 0.8880 | 1.4066 | 0.7016 | 0.9420 | 1.050 | 1.4426 | 0.6923 | 0.8894 | 1.567 | 1.4005 | 0.6984 | 0.8946 | 1.518 | 1.3960 | 0.6986 |
| 0.8014 | 0.9038 | 1.4060 | 0.7949 | 0.9402 | 1.000 | 1.4310 | 0.7987 | 0.9010 | 1.567 | 1.4005 | 0.8009 | 0.8974 | 1.566 | 1.3989 | 0.8029 |
| 0.8980 | 0.9189 | 1.4050 | 0.8987 | 0.9376 | 0.950 | 1.4182 | 0.8853 | 0.9101 | 1.578 | 1.4010 | 0.9017 | 0.9101 | 1.575 | 1.4005 | 0.9000 |
| 1.0000 | 0.9356 | 1.4040 | 1.0000 | 0.9356 | 0.914 | 1.4040 | 1.0000 | 0.9215 | 1.644 | 1.4042 | 1.0000 | 0.9215 | 1.644 | 1.4042 | 1.0000 |
| 308.15 K | | | | | | | | | | | | | | | |
| 0.0000 | 0.7643 | 1.4128 | 0.0000 | 0.9570 | 1.612 | 1.5352 | 0.0000 | 0.7914 | 1.486 | 1.3799 | 0.0000 | 0.7720 | 1.494 | 1.3706 | 0.0000 |
| 0.0981 | 0.7804 | 1.4153 | 0.1028 | 0.9542 | 1.472 | 1.5204 | 0.0969 | 0.8068 | 1.431 | 1.3816 | 0.1024 | 0.7903 | 1.404 | 1.3751 | 0.1017 |
| 0.1885 | 0.7960 | 1.4119 | 0.1977 | 0.9510 | 1.355 | 1.5070 | 0.1990 | 0.8221 | 1.395 | 1.3840 | 0.2002 | 0.8065 | 1.356 | 1.3786 | 0.2007 |
| 0.2854 | 0.8126 | 1.4096 | 0.3019 | 0.9478 | 1.249 | 1.4932 | 0.2917 | 0.8353 | 1.376 | 1.3869 | 0.3010 | 0.8228 | 1.324 | 1.3813 | 0.2996 |
| 0.3996 | 0.8317 | 1.4071 | 0.3993 | 0.9452 | 1.170 | 1.4794 | 0.3971 | 0.8495 | 1.326 | 1.3899 | 0.4035 | 0.8385 | 1.325 | 1.3854 | 0.4028 |
| 0.5024 | 0.8499 | 1.4062 | 0.5009 | 0.9425 | 1.087 | 1.4662 | 0.4928 | 0.8614 | 1.366 | 1.3924 | 0.5037 | 0.8531 | 1.329 | 1.3877 | 0.5032 |
| 0.6005 | 0.8662 | 1.4045 | 0.6660 | 0.9383 | 0.984 | 1.4450 | 0.5933 | 0.8736 | 1.377 | 1.3950 | 0.6022 | 0.8669 | 1.340 | 1.3914 | 0.6036 |
| 0.7027 | 0.8830 | 1.4041 | 0.7016 | 0.9372 | 0.967 | 1.4409 | 0.6923 | 0.8849 | 1.386 | 1.3960 | 0.6984 | 0.8798 | 1.360 | 1.3943 | 0.6986 |
| 0.8014 | 0.8988 | 1.4039 | 0.7949 | 0.9353 | 0.922 | 1.4291 | 0.7987 | 0.8964 | 1.403 | 1.3988 | 0.8009 | 0.8927 | 1.398 | 1.3975 | 0.8029 |
| 0.8980 | 0.9139 | 1.4034 | 0.8987 | 0.9326 | 0.879 | 1.4158 | 0.8853 | 0.9054 | 1.418 | 1.3992 | 0.9017 | 0.9054 | 1.413 | 1.3983 | 0.9000 |
| 1.0000 | 0.9301 | 1.4017 | 1.0000 | 0.9301 | 0.842 | 1.4017 | 1.0000 | 0.9168 | 1.471 | 1.4025 | 1.0000 | 0.9168 | 1.471 | 1.4025 | 1.0000 |
| 313.15 K | | | | | | | | | | | | | | | |
| 0.0000 | 0.7531 | 1.4173 | 0.0000 | 0.9531 | 1.473 | 1.5330 | 0.0000 | 0.7875 | 1.319 | 1.3776 | 0.0000 | 0.7674 | 1.287 | 1.3689 | 0.0000 |
| 0.0981 | 0.7692 | 1.4158 | 0.1028 | 0.9502 | 1.348 | 1.5182 | 0.0969 | 0.8027 | 1.272 | 1.3798 | 0.1024 | 0.7857 | 1.233 | 1.3726 | 0.1017 |
| 0.1885 | 0.7854 | 1.4144 | 0.1977 | 0.9470 | 1.245 | 1.5047 | 0.1990 | 0.8179 | 1.244 | 1.3823 | 0.2002 | 0.8021 | 1.190 | 1.3766 | 0.2007 |
| 0.2854 | 0.8010 | 1.4119 | 0.3019 | 0.9437 | 1.150 | 1.4909 | 0.2917 | 0.8310 | 1.235 | 1.3849 | 0.3010 | 0.8183 | 1.170 | 1.3802 | 0.2996 |
| 0.3996 | 0.8176 | 1.4096 | 0.3993 | 0.9409 | 1.078 | 1.4772 | 0.3971 | 0.8452 | 1.178 | 1.3877 | 0.4035 | 0.8340 | 1.176 | 1.3837 | 0.4028 |
| 0.5024 | 0.8354 | 1.4071 | 0.5009 | 0.9381 | 1.004 | 1.4638 | 0.4928 | 0.8571 | 1.223 | 1.3901 | 0.5037 | 0.8486 | 1.190 | 1.3867 | 0.5032 |
| 0.6005 | 0.8549 | 1.4062 | 0.6660 | 0.9353 | 0.913 | 1.4427 | 0.5933 | 0.8693 | 1.233 | 1.3918 | 0.6022 | 0.8624 | 1.203 | 1.3900 | 0.6036 |
| 0.7027 | 0.8712 | 1.4060 | 0.7016 | 0.9326 | 0.897 | 1.4389 | 0.6923 | 0.8804 | 1.232 | 1.3944 | 0.6984 | 0.8753 | 1.217 | 1.3911 | 0.6986 |
| 0.8014 | 0.8880 | 1.4050 | 0.7949 | 0.9305 | 0.859 | 1.4267 | 0.7987 | 0.8919 | 1.265 | 1.3957 | 0.8009 | 0.8882 | 1.259 | 1.3952 | 0.8029 |
| 0.8980 | 0.9038 | 1.4040 | 0.8987 | 0.9278 | 0.815 | 1.4137 | 0.8853 | 0.9008 | 1.402 | 1.3970 | 0.9017 | 0.9009 | 1.267 | 1.3964 | 0.9000 |
| 1.0000 | 0.9257 | 1.4017 | 1.0000 | 0.9257 | 0.786 | 1.3992 | 1.0000 | 0.9125 | 1.333 | 1.4003 | 1.0000 | 0.9125 | 1.333 | 1.4003 | 1.0000 |

Table 3. Estimated Parameters of Mixing Functions for Binary Mixtures at Different Temperatures

| <i>T</i> /K | <i>A</i> ₀ | <i>A</i> ₁ | <i>A</i> ₂ | <i>A</i> ₃ | <i>A</i> ₄ | σ | <i>T</i> /K | <i>A</i> ₀ | <i>A</i> ₁ | <i>A</i> ₂ | <i>A</i> ₃ | <i>A</i> ₄ | σ |
|--|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|----------|---------------------------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|----------|
| Diglyme (1) + Cyclohexane (2) | | | | | | | 2-Ethoxyethanol (1) + Propan-2-ol (2) | | | | | | |
| $V^E/\text{cm}^3\text{mol}^{-1}$ | | | | | | | $V^E/\text{cm}^3\text{mol}^{-1}$ | | | | | | |
| 298.15 | 5.156 | 4.109 | 5.992 | -4.923 | -8.916 | 0.180 | 298.15 | 0.031 | 0.046 | 0.016 | 0.088 | 0.115 | 0.013 |
| 303.15 | 5.801 | 4.925 | 4.682 | -7.243 | -6.796 | 0.151 | 303.15 | 0.068 | 0.069 | 0.422 | -0.007 | -0.765 | 0.017 |
| 308.15 | 5.470 | 4.401 | 5.667 | -5.330 | -8.326 | 0.165 | 308.15 | 0.056 | 0.047 | 0.454 | -0.105 | -1.052 | 0.012 |
| | | | | | | | 313.15 | 0.092 | -0.046 | 0.349 | -0.143 | -0.643 | 0.011 |
| $\Delta\eta/\text{mPa}\cdot\text{s}$ | | | | | | | $\Delta\eta/\text{mPa}\cdot\text{s}$ | | | | | | |
| 298.15 | -0.598 | -0.188 | -0.158 | -0.160 | -0.327 | 0.001 | 298.15 | -0.818 | -0.376 | -0.126 | 0.548 | 0.317 | 0.008 |
| 303.15 | -0.307 | -0.046 | -0.230 | 0.552 | 0.685 | 0.006 | 303.15 | -0.796 | -0.411 | -0.139 | 0.236 | -0.257 | 0.010 |
| 308.15 | -0.270 | -0.073 | -0.116 | 0.530 | 0.610 | 0.005 | 308.15 | -0.624 | -0.288 | -0.074 | 0.113 | -0.292 | 0.005 |
| | | | | | | | 313.15 | -0.496 | -0.262 | -0.176 | 0.354 | -0.068 | 0.008 |
| $\Delta R/\text{cm}^3\text{mol}^{-1}$ | | | | | | | $\Delta R/\text{cm}^3\text{mol}^{-1}$ | | | | | | |
| 298.15 | -1.381 | -0.932 | 0.705 | 2.116 | -0.392 | 0.063 | 298.15 | -1.422 | 0.028 | 1.461 | -0.828 | -2.368 | 0.079 |
| 303.15 | -0.961 | -1.207 | 0.341 | 1.302 | 1.275 | 0.057 | 303.15 | -1.538 | -0.120 | 0.918 | -0.516 | -1.843 | 0.018 |
| 308.15 | -0.622 | -1.622 | 0.193 | 0.703 | 3.468 | 0.064 | 308.15 | -1.563 | -0.036 | 1.475 | -0.824 | -2.744 | 0.028 |
| | | | | | | | 313.15 | -1.360 | -0.208 | -0.058 | -0.299 | -1.003 | 0.048 |
| Diglyme (1) + 1,2,3,4-Tetrahydronaphthalene (2) | | | | | | | 2-Ethoxyethanol (1) + Butan-1-ol (2) | | | | | | |
| $V^E/\text{cm}^3\text{mol}^{-1}$ | | | | | | | $V^E/\text{cm}^3\text{mol}^{-1}$ | | | | | | |
| 298.15 | 0.376 | 0.383 | -0.341 | -0.552 | 0.024 | 0.033 | 298.15 | 0.137 | 0.149 | 0.171 | 0.025 | -0.208 | 0.031 |
| 303.15 | 0.566 | 0.160 | 0.426 | -0.652 | -0.882 | 0.029 | 303.15 | 0.234 | 0.112 | 0.288 | 0.304 | -0.455 | 0.040 |
| 308.15 | 0.418 | 0.288 | 0.425 | -0.565 | -1.666 | 0.027 | 308.15 | 0.255 | 0.023 | -0.080 | 0.377 | 0.077 | 0.046 |
| 313.15 | 0.541 | 0.103 | 0.308 | -0.890 | -1.026 | 0.024 | 313.15 | 0.306 | 0.062 | 0.254 | 0.178 | 0.086 | 0.031 |
| $\Delta\eta/\text{mPa}\cdot\text{s}$ | | | | | | | $\Delta\eta/\text{mPa}\cdot\text{s}$ | | | | | | |
| 298.15 | -0.707 | -0.319 | -0.058 | 0.300 | -0.089 | 0.011 | 298.15 | -1.104 | -0.495 | -0.351 | -0.050 | 0.048 | 0.007 |
| 303.15 | -0.632 | -0.169 | -0.105 | 0.054 | 0.094 | 0.002 | 303.15 | -0.956 | -0.360 | -0.089 | -0.169 | -0.347 | 0.007 |
| 308.15 | -0.547 | -0.130 | -0.091 | -0.025 | 0.107 | 0.003 | 308.15 | -0.780 | -0.288 | -0.228 | -0.135 | 0.047 | 0.006 |
| 313.15 | -0.493 | -0.124 | -0.017 | 0.012 | -0.029 | 0.002 | 313.15 | -0.700 | -0.230 | 0.031 | -0.057 | -0.491 | 0.006 |
| $\Delta R/\text{cm}^3\text{mol}^{-1}$ | | | | | | | $\Delta R/\text{cm}^3\text{mol}^{-1}$ | | | | | | |
| 298.15 | 0.872 | 0.145 | 0.522 | 1.221 | 0.019 | 0.018 | 298.15 | -0.223 | -0.063 | 0.327 | 0.064 | -0.459 | 0.050 |
| 303.15 | 0.820 | -0.030 | 0.922 | 1.579 | -0.341 | 0.021 | 303.15 | -0.256 | 0.093 | 1.046 | -0.548 | -1.573 | 0.047 |
| 308.15 | 0.803 | 0.238 | 1.336 | 1.149 | -1.218 | 0.019 | 308.15 | -0.235 | -0.022 | 0.108 | -0.844 | -0.195 | 0.051 |
| 313.15 | 0.889 | 0.367 | 1.058 | 1.195 | -0.434 | 0.026 | 313.15 | -0.220 | -0.067 | 0.739 | -0.762 | -0.798 | 0.039 |
| 2-Ethoxyethanol (1) + Propan-1-ol (2) | | | | | | | | | | | | | |
| $V^E/\text{cm}^3\text{mol}^{-1}$ | | | | | | | | | | | | | |
| 298.15 | -0.205 | -0.070 | 0.387 | 0.120 | -0.352 | 0.013 | | | | | | | |
| 303.15 | -0.140 | -0.165 | 0.403 | 0.104 | -0.683 | 0.006 | | | | | | | |
| 308.15 | -0.095 | -0.096 | -0.107 | -0.001 | 0.231 | 0.012 | | | | | | | |
| 313.15 | -0.012 | -0.112 | 0.082 | -0.163 | 0.403 | 0.008 | | | | | | | |
| $\Delta\eta/\text{mPa}\cdot\text{s}$ | | | | | | | | | | | | | |
| 298.15 | -0.695 | -0.417 | 0.225 | 0.618 | -0.612 | 0.032 | | | | | | | |
| 303.15 | -0.607 | -0.335 | 0.332 | 0.546 | -0.851 | 0.024 | | | | | | | |
| 308.15 | -0.497 | -0.299 | 0.196 | 0.508 | -0.530 | 0.023 | | | | | | | |
| 313.15 | -0.438 | 0.142 | -0.741 | -1.253 | 2.522 | 0.040 | | | | | | | |
| $\Delta R/\text{cm}^3\text{mol}^{-1}$ | | | | | | | | | | | | | |
| 298.15 | -1.691 | -0.102 | 0.388 | 0.102 | -0.840 | 0.047 | | | | | | | |
| 303.15 | -1.682 | 0.191 | -0.114 | -0.713 | -0.789 | 0.016 | | | | | | | |
| 308.15 | -1.699 | 0.193 | -0.389 | -0.639 | -0.434 | 0.028 | | | | | | | |
| 313.15 | -1.704 | -0.081 | -0.085 | -0.574 | -0.713 | 0.023 | | | | | | | |

Stanley Ltd., London). Triplicate measurements in refractive index are accurate to ± 0.0001 unit. Experimental details of measurements of ρ , η , and n_D are the same as given earlier (23).

In all property measurements, an INSREF, Model 016 AP, thermostat was used at a constant temperature control of ± 0.01 K with a digital display. Binary data compiled in Table 2 are the averages of at least three independent measurements for each composition.

Results and Discussion

Excess molar volumes of the mixtures were calculated from density data using

$$V^E/(\text{cm}^3\text{mol}^{-1}) = V_m - V_1x_1 - V_2x_2 \quad (1)$$

where V_1 , V_2 , and V_m are molar volumes of components 1 and 2 and the mixture, respectively, and x_1 and x_2 represent the mole fractions of components 1 and 2, respectively.

The deviations in viscosity $\Delta\eta$ and molar refractivity ΔR were calculated using the general relation

$$\Delta Y = Y_m - Y_1C_1 - Y_2C_2 \quad (2)$$

where ΔY refers to $\Delta\eta/\text{mPa}\cdot\text{s}$ and ΔR , respectively; Y_m is the measured mixture property under question, and Y_i refers to property of the pure components. The terms C_1 and C_2 are mixture compositions expressed as mole fraction for the calculation of $\Delta\eta$ and volume fraction, ϕ_i , for ΔR .

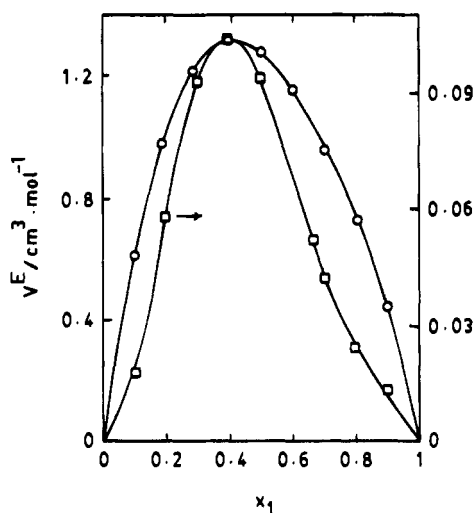


Figure 1. Excess molar volume for mixtures of diglyme with (○) cyclohexane and (□) 1,2,3,4-tetrahydronaphthalene at 298.15 K.

The volume fraction was calculated as

$$\phi_i = x_i V_i / \sum_{i=1}^2 x_i V_i \quad (3)$$

The calculated values of V^E , $\Delta\eta$, and ΔR were fitted to a Redlich-Kister polynomial (12) relation:

$$\Delta Y \text{ or } V^E = C_1 C_2 \sum_{i=0}^4 A_i (C_2 - C_1)^i \quad (4)$$

The parameter estimations were done using the Marquardt algorithm (13). In this algorithm, we consider the fitting when the model depends nonlinearly on a set of M unknown parameters A_k , with $k = 1, 2, \dots, M$, to determine its best-fit parameters by minimization through the iterative procedure. Given the trial values for the parameters, we have developed a procedure that improves the trial solution. This procedure was repeated until the best fit was achieved. For all mixtures, the precision warrants the use of five adjustable parameters at 95% confidence level.

Standard errors, σ , between the calculated and the experimental values were estimated as

$$\sigma(\Delta Y \text{ or } V^E) = \left[\sum_{i=1}^m \{(\Delta Y \text{ or } V^E)_{\text{exptl}} - (\Delta Y \text{ or } V^E)_{\text{calcd}}\}^2 / (m - p) \right]^{1/2} \quad (5)$$

where m is the number of data points and p is the number of estimated parameters. The results of A_i and σ are presented in Table 3.

The results of V^E at 298.15 K for mixtures of diglyme with cyclohexane or 1,2,3,4-tetrahydronaphthalene are given in Figure 1. It is found that for both mixtures the values of V^E are positive, suggesting mild dispersion-type interactions. However, the V^E values for the diglyme + cyclohexane mixture are higher by an order of magnitude than those for the diglyme + 1,2,3,4-tetrahydronaphthalene mixture, suggesting smaller volume expansion in the presence of the larger 1,2,3,4-tetrahydronaphthalene molecule as compared with cyclohexane. The values of $\Delta\eta$ presented at 298.15 K in Figure 2 are negative for both diglyme + cyclohexane and diglyme + 1,2,3,4-tetrahydronaphthalene mixtures. The $\Delta\eta$ values are more nega-

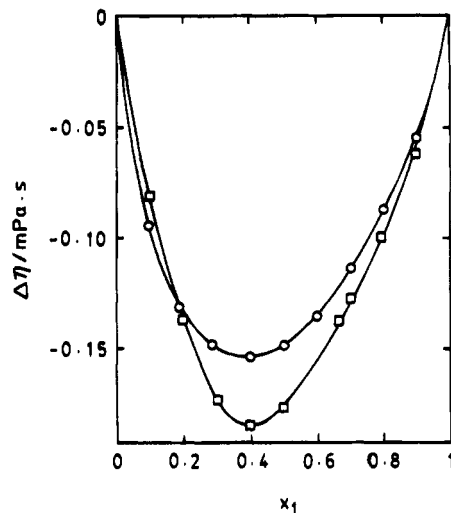


Figure 2. Deviation in viscosity at 298.15 K for the same mixtures given in Figure 1.

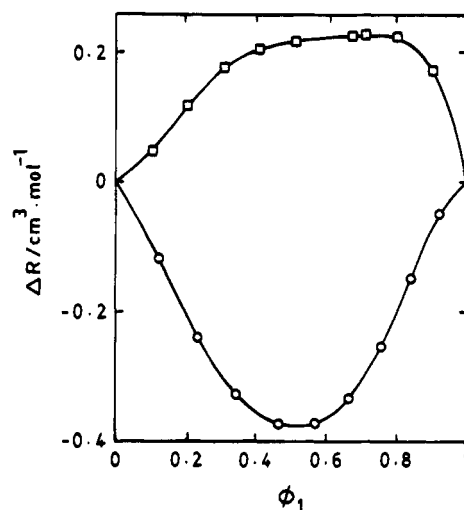


Figure 3. Deviation in molar refractivity at 298.15 K for the same mixtures given in Figure 1.

tive for the latter mixture when compared to the former. On the other hand, the results of ΔR versus volume fraction, ϕ_1 , of diglyme at 298.15 K, shown in Figure 3, are positive for the diglyme + 1,2,3,4-tetrahydronaphthalene mixture and negative for the diglyme + cyclohexane mixture.

The V^E results for mixtures of 2-ethoxyethanol with propan-1-ol, propan-2-ol, or butan-1-ol at 298.15 K are small and vary between -0.055 and 0.050 $\text{cm}^3 \cdot \text{mol}^{-1}$ (Figure 4). Negative values of V^E are observed for 2-ethoxyethanol + propan-1-ol, whereas mixtures of 2-ethoxyethanol + propan-2-ol or butan-1-ol exhibit positive V^E ; the curves for these mixtures are somewhat skewed toward the 2-ethoxyethanol-poor region of the mixtures. However, the V^E values of these mixtures increase with the size of the alkanol from propan-1-ol to butan-1-ol via propan-2-ol, suggesting a decrease in specific interactions with increasing size of the alkanol. The results of $\Delta\eta$ for the alkanol mixtures with 2-ethoxyethanol at 298.15 K are negative, as shown in Figure 5. These negative values increase with increasing size of the alkanol in the mixture. The dependence of ΔR on ϕ_1 at 298.15 K is displayed in Figure 6, wherein the negative values are observed for all of the alkanol-containing 2-ethoxyethanol mixtures. The results of ΔR increase in the order propan-1-ol < propan-2-ol < butan-1-ol. This trend is the reverse of that observed for $\Delta\eta$ versus x_1 plots shown in Figure 5.

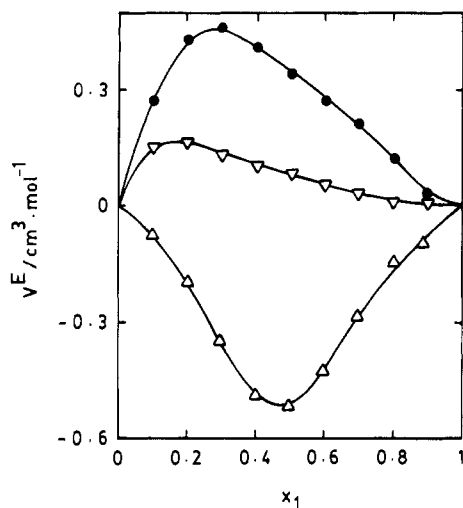


Figure 4. Excess molar volume at 298.15 K for mixtures of 2-ethoxyethanol with (Δ) propan-1-ol, (∇) propan-2-ol, and (\bullet) butan-1-ol.

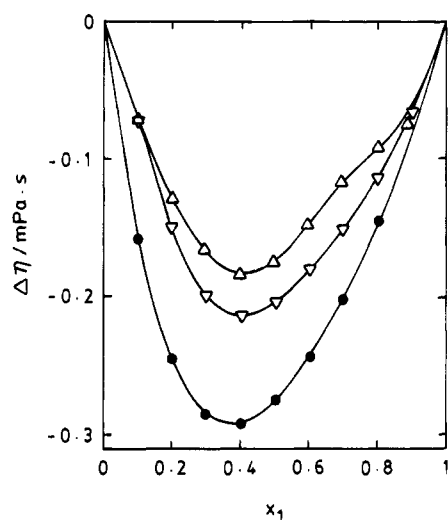


Figure 5. Deviation in viscosity at 298.15 K for the same mixtures given in Figure 4.

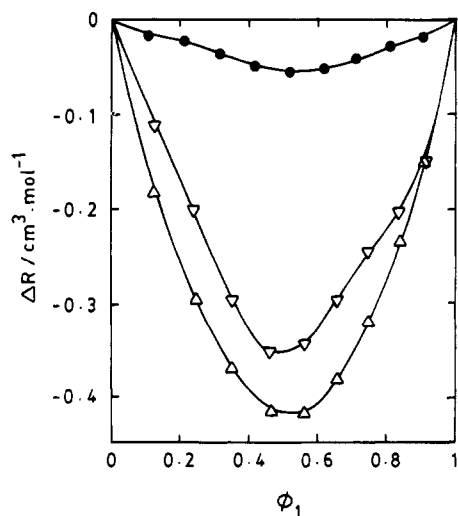


Figure 6. Deviation in molar refractivity at 298.15 K for the same mixtures given in Figure 4.

The equimolar values of V^E , $\Delta\eta$, and ΔR for the extreme temperatures are presented in Table 4. It is observed that for all mixtures the values of V^E increase with increasing

Table 4. Equimolar Values of V^E , $\Delta\eta$, and ΔR

| mixture | T/K | $V^E/(\text{cm}^3\cdot\text{mol}^{-1})$ | $\Delta\eta/(\text{mPa}\cdot\text{s})$ | $\Delta R/(\text{cm}^3\cdot\text{mol}^{-1})$ |
|---|--------|---|--|--|
| diglyme + cyclohexane | 298.15 | 1.289 | -0.150 | -0.339 |
| diglyme + cyclohexane | 308.15 | 1.368 | -0.068 | -0.153 |
| diglyme + 1,2,3,4-tetrahydronaphthalene | 298.15 | 0.092 | 0.177 | 0.218 |
| diglyme + 1,2,3,4-tetrahydronaphthalene | 313.15 | 0.135 | 0.123 | 0.222 |
| 2-ethoxyethanol + propan-1-ol | 298.15 | -0.054 | -0.174 | -0.417 |
| 2-ethoxyethanol + propan-1-ol | 313.15 | -0.003 | -0.110 | -0.420 |
| 2-ethoxyethanol + propan-2-ol | 298.15 | -0.003 | -0.205 | -0.357 |
| 2-ethoxyethanol + propan-2-ol | 313.15 | 0.023 | -0.124 | -0.335 |
| 2-ethoxyethanol + butan-1-ol | 298.15 | 0.038 | -0.313 | -0.058 |
| 2-ethoxyethanol + butan-1-ol | 313.15 | 0.087 | -0.199 | -0.055 |

temperature and that the V^E values for mixtures of diglyme + cyclohexane are higher by an order of magnitude than observed for the diglyme + 1,2,3,4-tetrahydronaphthalene mixture. For mixtures containing 2-ethoxyethanol, the V^E values are negative in the case of propan-1-ol at all temperatures, whereas positive values of V^E are observed for mixtures of 2-ethoxyethanol + propan-2-ol or butan-1-ol. The observed positive values for the latter mixtures are smaller than for diglyme-containing mixtures. Both $\Delta\eta$ and ΔR values for all three mixtures of alkanols + 2-ethoxyethanol are negative at all temperatures.

A considerable amount of work on the thermodynamic properties of binary systems formed by mixing alkanols with n -alkanes has been done to understand the thermodynamic behavior of these systems (24). In all of these studies, V^E values are positive and increase with either an increase in side methyl group substitution or an increase in hydroxy groups of alkanols. However, an opposite behavior is observed with the present 2-ethoxyethanol + alkanol mixtures. On the other hand, with alkanol + alkanol mixtures, it has been generally observed that the values of $\Delta\eta$ are negative and those of V^E are small but increase with increasing length of alkanols (25). This trend is similar to that observed in the present study.

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Received for review August 26, 1994. Revised November 23, 1994.
Accepted November 27, 1994.*

JE940178Z

* Abstract published in *Advance ACS Abstracts*, January 1, 1995.